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TWO YEARS OF INDUSTRIAL OPHTHALMOLOGY AT THE PULLMAN CAR WORKS*

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IN January, 1923, the Pullman Company established a half-time oculist in its dispensary at the manufacturing plant at Pullman. The duties of the oculist are:

1. To take visual acuity and pass judgment on the advisability of hiring men who request employment.

2. To examine the eyes of train crews, electric locomotive and monorail crane operators.

3. To test for errors in refraction and to order prescriptive goggles.

4. To treat injuries to the eyes.

5. To treat eye diseases.

The oculist has a dark room fitted with the usual ophthalmologic equipment. This room adjoins the main dispensary, which is centrally located within reach of the different departments and shops of the plant, and to which the men come to be classified. Those who are to visit the oculist are sent in with a card bearing their names, departments, check numbers, and addresses. This card is 4 by 6 inches, and it also has provision for the diagnosis, complaint, and eye findings (see Figs. 1 and 2). When this is full a plain card is pinned to the original. The nature of the case (medical or injury) is indicated on the card by a small check. If an industrial injury case, for which the Company may be liable, a fuller report is made out for the legal and safety departments on a separate form. All injuries received outside the plant are classified as medical cases. Naturally, the oculist sees a good many injuries which are classified as medical cases in this report.

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Examination of Applicants

There are from 8,000 to 10,000 employees on the payroll at all times, and the labor turnover amounts to from 900 to 3,500 men a month. Accordingly, it is impossible to examine the eyes of all the men hired. However, the oculist sees all the men who wear glasses, all men over 40 years of age, and all men who have any visible eye defects.

The policy as to hiring new men excludes those with only one eye. One-eyed men now employed are retained, but they must wear side-screened goggles at all times while in the plant. They are granted leave of absence on request, but should they leave of their own accord, without sickness, they are not rehired. All new men who have less than 20/200 vision without glasses in one eye are not rehired, even though their vision can be corrected to 20/20 with glasses. Our hiring age limit[1] rules out the elderly men, and the only cases this affects are the higher myopes, and, of course, those with old injuries, some with amblyopia and mal developments, and very high hyperopes. The 20/200 clause is the result of the Illinois Industrial Act which makes a man industrially blind when his vision is under 20/200. We have many old-timers who are industrially blind without glasses and practically normal with glasses. These men, of course, are given prescriptive goggles, with bifocals when necessary, for constant wear in the shop.

[1] "No person 55 years of age or over may be taken into service as a new employe of the Corporation except by special authority of the President, obtained prior to such employment: no person between the ages of 45 and 55 years taken into service as a new employe, shall be retained beyond the next ensuing pay period without authorization from the President for retention."

Examination of Train Crews

Railroad standard vision is required for our railroad employees, for our train crews, and for our electric locomotive and monorail crane operators. As the monorail crane operators have to be over steam one minute and exposed to hot or cold air another, we do not find it practicable for them to wear goggles. They are far too high for danger to themselves, and we insist on their vision being good so that they will not injure anyone below; with steamy goggles, this might happen. All these men have 20/20 in both eyes without glasses.

Safety Goggles

Let us now follow John Doe, Ck. No. 100, from the firing line to the base hospital. John is given a job as laborer in the freight shop. He has been instructed by his foreman as to the nature of his work, and is given his tools and a pair of plano, superarmor-plate goggles with side screens. Everything goes well until the fifth day. John takes off his goggles to "wipe them" and something hits him in the eye. He is immediately taken to the first-aid station where the nurse (R. N.) discovers a foreign body on the cornea of the left eye. His eye is cleansed and bandaged. He rides to the dispensary where it is removed and proper treatment instituted by the oculist. He returns to work three days later.

Suppose that John does not like to wear goggles and discards them. In

LAST NAME FIRST NAME

CK. NO. DATE

Occup. Dept. Addr.

Age Sex Civil State Race Nationality

COMPLAINT

DIAGNOSIS	R.	Medical ☐ Injury ☐	L.
Vision			
Vis. { Spect's ☐ Goggles ☐			
Eyelids			
Conjunctiva			
Cornea			
Iris			
Lens			
Fundus			

FORM 81.84 Injury No. EYE EXAMINATION RECORD

FIG. 1.—Front of eye examination record card (slightly reduced).

REFRACTION:—H & C—E & C—Mnfst.—

DATE:

℞ R.
L.

Add for near R. & L.

ORDER

☐ Distance
☐ Near
☐ Bifocal
☐ Work
In-Goggle, A-B-C-D-E-F
P. D.

RETINOSCOPY

R L.

Remarks:

FIG. 2.—Upper part of back of record card. The lower part is blank, and therefore is not reproduced.

half an hour, he is stopped by the safety inspector and is told why he should wear them. He promises to do so, but is caught without them the next day. He says that the goggles steam up and that they give him headaches. He is sent to the oculist who gives him a prescriptive, super-armor-plate pair of goggles. He is relieved of headaches and wears his goggles most of the time. Two months later, a piece of steel hits his goggles, bending them up and cracking the lenses, but his eyes are not injured. John is a safety-first man for life and will not go back to work until he has new goggles. The safety inspector is his best friend.

Employees are allowed to visit the oculist whenever they desire "on pass," but they must first get permission from the "leader." In case of any injury, however, the nearest fellow workman takes the injured man to the dispensary at once.

We use several types of goggles. They are 46 mm. round, are made like spectacles, and protect the eyes and upper cheek. Some have no side screens, while others have. The side screens keep dust and particles from coming in around the back of the lens. They envelop the eye with a metal screen on all sides. For sand blasters, a finer mesh is used on the side screens. These are called dust-proof goggles. In extremely dusty places, rubberoid goggles are used which protect the eyes more fully. They are held on by means of an adjustable elastic band around the back of the head. For arc welders, the rubber goggles are used with a suitable color to cut out the ultraviolet rays. The lenses are 3 mm. thick and withstand a good blow. When the blow is heavy enough to break the lens, the lens shatters inside the goggles without leaving the frame. These lenses can be ground in any reasonable strength and are given to the men on "ticket" without cost to them, just as their tools are issued to them. Their names are stamped on the goggle frame bar so that they will know their own goggles, and they are instructed never to lend them to another. This keeps down infections and skin diseases.

In the beginning, there was difficulty in educating the men to wear goggles. They considered it an encroachment on their personal liberties and invariably said that they had worked for the Company for twenty years or more and had never had an eye injury. In order to convince them of the necessity for wearing goggles, posters were placarded throughout the plant giving the names of some of their own men whose goggles had saved their eyesight. Then, the leaders and superintendents set the example, and gradually the men saw the point. At first, goggles without side screens were given but they are now being replaced with the side-screened goggles.

Our greatest difficulty has been in overcoming the complaints that the goggles are too heavy, that they cause headaches, that the lenses steam up, and that the side screen cuts off side vision. These points were finally cleared by individual talks and by fitting the employee to his individual need. At first, some men absolutely refused to wear the goggles and became defiant. One or two of these were sent elsewhere to find jobs. On the whole, however, the employees have been co-operative.

Care of Injuries

There are two first-aid stations where registered nurses are on duty. In this way, patients with acid burns and serious injuries are given first aid and sterile dressing before being sent to the central dispensary. The men are instructed to keep soiled handkerchiefs, knives, toothpicks, flaxseeds, and human tongues out of an injured eye. Flaxseeds are used extensively by negroes and the human tongue by foreigners when attempting to remove foreign substances.

The oculist sees every variety of eye disease that is seen in private offices and in public dispensaries, and

often gives advice to the employee about his general health, for, as is well known, ophthalmology and general medicine go hand in hand. Among the unusual injuries, the following are recalled:

A baby scratched its father's eye with its finger nail.

A man scratched his eye on a gooseberry bush.

A girl let a hot curling iron slip and it struck her eye.

A man blew his breath into a coffee percolator and splashed hot coffee into his eyes.

A man put tincture of iodine in his eyes, mistaking it for argyrol.

An icicle fell off a roof striking a man's eye.

A man, while sleeping, scratched his cornea with his wife's hairpin—there was no wound on the lid, but that is the story he told.

Twice as many injuries to the eyes occur at 4:30 P.M. as occur at any other time of day. This can be explained by fatigue, by waning illumination, and by the desire to finish tasks by quitting time. More injuries occur in proportion to the number employed when the plant is rushed with orders than when orders are slack and the men work more leisurely. There are fewer visits on Tuesdays and Thursdays than on any other days of the week. Why this happens cannot be explained, for no reason can be given why the workmen should be less careful on certain days of the week.

Analysis of Data

Below is a tabulation of the cases seen in two years:

	Number	*Per Cent.*
For hiring	875	15.8
Refractions	2,285	41.4
Industrial injuries	1,455	26.3
Medical	915	16.5
Total new cases	5,530	100.0
Revisits	2,404	
Total cases seen	7,934	

Of the 1,455 industrial injuries seen, the vast majority have been foreign bodies in the eyes, but there have also been some serious injuries, such as burns, contusions, and penetrations by steel, needles, and other foreign substances. In spite of our vigorous goggle campaign, a little over one-fourth of all the cases seen by the oculist have been injuries to the eyes. Fortunately, the foreign bodies have been removed early, so that the loss in vision and eyes has been negligible as compared to what it would have been had there been delay.

In Table 1 the first 4,000 cases seen consecutively are tabulated according to vision without any corrective lenses being placed before the eyes. In analyzing the record of these consecutive tests of vision, the worse eye was always tabulated. For example, a man may have an amblyopia in one eye with vision of 20/200, while the other eye is normal. This case would go under the 20/200 tabulation. There is one other item that needs explanation, and that is the 17.4 per cent. who have only 20/200 vision. This class includes many men around 60 years of age whose vision can be brought up to about 20/30 by lenses. It also contains some cases of amblyopia which cannot be improved.

Table 1 shows 1,139 cases of normal vision and 2,861 cases of subnormal vision, equal to 28.5 per cent. and 71.5

per cent., respectively, of the total 4,000 cases. Many of the 2,861 subnormal visions can be improved by lenses. These cases are tabulated separately on this basis in Table 2.

TABLE 1.—TABULATION OF 4,000 CASES ACCORDING TO VISION WITHOUT CORRECTIVE LENSES

NUMBER	PER CENT.	VISION WITHOUT LENSES
1,139	28.48	normal (20/20 to 20/15)
1,151	28.77	92%[1] (20/25 to 20/30)
298	7.45	85%[1] (20/40)
246	6.15	79%[1] (20/50)
229	5.73	66%[1] (20/70)
190	4.75	35%[1] (20/100)
696	17.40	5%[1] (20/200)
51	1.27	only one eye

[1] From the Chicago Ophthalmological Society and State of Wisconsin Tables of Compensation for Loss of Vision.

Further analysis of the 4,000 cases gives the following results: 1,139 cases, or 28.5 per cent., have normal vision without lenses, and 400 cases, or 10 per cent., can be brought to normal by lenses. This makes a total of 38.5 per cent. who are or can be made normal, leaving 61.5 per cent. who cannot be made normal by glasses.

Some of these men are "letter ignorant" and the exact status of their visual acuity is difficult to determine. If we accept 20/30 as near enough to normal vision for practical purposes, we have 2,290, or 57.25 per cent., who have good vision without lenses. This, of course, gives a rosier picture. Still, it is hard to say that all of these men are "letter ignorant;" some undoubtedly are, but many have defective eyesight. In this series, no effort was made to differentiate between "letter ignorant," beginning sclerosis of the lens in senile eyes, scars of the cornea, cataracts, and fundus lesions. The vision was the tabulating factor, regardless of the etiology of the loss of vision.

TABLE 2.—TABULATION OF 2,861 CASES OF SUBNORMAL VISION ON THE BASIS OF THE IMPROVEMENT POSSIBLE WITH LENSES

NUMBER	PER CENT.	VISION WITH LENSES
400	14.0	normal (20/20 to 20/15)
465	16.2	92%[1] (20/25 to 20/30)
129	4.5	85%[1] (20/40)
66	2.3	79%[1] (20/50)
53	1.9	66%[1] (20/70)
28	1.0	35%[1] (20/100)
1,141	39.9	more or less improvement possible
1,720	60.1	cannot be improved by lenses

[1] From the Chicago Ophthalmological Society and State of Wisconsin Tables of Compensation for Loss of Vision.

Some of the original 4,000 patients who had normal vision have lost their good vision. For example, one man developed optic atrophy and lost most all of his vision. Another "leader" lost his son and went on a protracted drinking party. He returned three months later with a vision of 7/200 with optic atrophy. He had an excellent record with the Company and wanted to begin again as a band sawyer. Needless to say, he was not safe on a saw with that vision.

One of the surprises in this series was a young albino who had nystagmus and wore highly astigmatic hyperopic lenses. With these lenses, he could get only 20/200 in either

eye. He was followed up, and his leader reported that he was one of the best cabinet makers in the shop. This man made up in feeling what he lacked in vision, but he is an exception to the rule. Most men with very poor vision are poor workmen.

Summary

1. Of 4,000 men consecutively examined 1,139, or 28.48 per cent., had normal vision in both eyes without lenses; 1,539, or 38.48 per cent., had normal vision in both eyes with lenses.

2. There is an appalling number of amblyopias, mal developments, and old injuries in the eyes of industrial employees.

3. The average employee has still to be educated as to the industrial eye hazard he takes without goggles.

4. The employee should be instructed that neglected cross-eyes and defective vision in his family are hazardous to eyesight conservation.

RECOMMENDATIONS FOR CONTROLLING HEALTH HAZARDS IN GARAGES AND AUTOMOBILE REPAIR SHOPS*

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COMPOSITION OF EXHAUST GAS

EXPERIMENTS with exhaust gas show it to contain a dangerous amount of carbon monoxide, sometimes as much as 15 per cent. Carbon monoxide is a colorless, odorless gas. It is present wherever incomplete burning or combustion takes place; in blast furnaces, in coal mines, and where blasting has been done; in bake ovens, in illuminating gas, and in exhaust gas from automobiles. When the carburetor of an automobile is adjusted to a "rich mixture," there is more carbon monoxide in the exhaust gas than with a thinner mixture.

Where motor fuel is wholly so-called "gasoline" distilled directly from petroleum, carbon monoxide, arising from incomplete combustion, is the only poison to fear. In some sections of the country, however, much more poisonous fuels are already in use, and because of their cheapness are practically certain to be used everywhere in the near future. In fuels adulterated with cracked petroleum, coal distillate, and other like materials, there is often a high content of benzol (benzene) and other poisonous coal tar products (1).

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Lead also may be present in exhaust gas where some of the new motor fuels are used.

Carbon Monoxide Poisoning

Carbon monoxide is dangerous to health and life, because it takes the place of oxygen in the blood. The more carbon monoxide there is in the blood, the less oxygen the blood will hold. Without oxygen life cannot go on.

"The gas victim becomes asphyxiated just as if he were being gradually choked to death. As low as one-tenth of 1 per cent. of carbon monoxide, or even less, in the air will kill a man in time; 1 per cent. will kill in a few minutes" (2).

Poisoning from carbon monoxide may be either acute—a matter of minutes—or subacute—slow. The latter is the result of frequent mild attacks of gassing. The type of poisoning depends on the amount of carbon monoxide in the air and the length of time the worker breathes this poisoned air.

Acute Poisoning.—When an engine "is run idle to warm it on a cold day with the garage doors closed, the atmosphere of a space large enough to hold a car is contaminated to a very dangerous extent (25 parts of carbon monoxid in

10,000 of air) within five minutes, and to a rapidly fatal extent in ten minutes." "The first indication that the victim receives is that his legs give way under him; he lies helpless until unconsciousness ceases a few minutes later; and in the accumulating gas, death by asphyxia follows unless chance brings help within a short period thereafter" (1). If rescued in time and revived by artificial means of breathing, men actually gassed may recover.

Among the after effects of gassing are a susceptibility to pneumonia; nervous conditions, such as loss of memory; and paralysis (most often of the legs). Blindness, deafness, loss of weight, and permanent weakening of the heart and other vital organs also may result (3).

Subacute Poisoning.—Conditions in public garages and repair shops are such as to produce many more cases of subacute than of acute poisoning. Few garages have any effective system of ventilation. Workers continuously exposed, even to small quantities of carbon monoxide, suffer from frequent mild attacks of gassing.

The symptoms are: headache, nausea, breathlessness, general nervousness, disturbed sleep, indigestion, loss of appetite, and acid belchings from the stomach. Studies show such symptoms to be an almost daily occurrence among garage employees. In the early stages of carbon monoxide poisoning there seems to be a loss of muscular power and of mental alertness, workers are irritable, and judgment is affected. The high accident rate in the trade is probably increased by this condition. Repeated attacks of subacute poisoning by carbon monoxide result in greatly lowered vitality which breaks down the power of the body to withstand disease.

Studies of Garage Workers in the United States

Several studies have been made in the United States proving the general occurrence of carbon monoxide poisoning among garage workers.

In December, 1920, the New York State Department of Labor (4) visited 1,308 garages and automobile repair shops, employing 5,906 men. No medical examinations were made but questions disclosed 113 cases of asphyxiation in two years. One hundred and fifty-five persons interviewed were suffering from headaches. Four hundred and forty-three cases of sickness were found, not directly traceable to carbon monoxide; seven deaths occurred in this group. There was a record of 208 accidents.

Dr. Alice Hamilton (5) conducted an investigation for the United States Department of Labor in the fall of 1921. Thirty-six of the fifty-five garage men examined, or 65.4 per cent., showed carbon monoxide in the blood.

More recently, in November, 1923, Dr. Ciampolini (6) inspected 157 garages for the New York State Department of Labor. He tested the blood of forty-two workers and found carbon monoxide in 69.5 per cent. Of the garages inspected, 77.5 per cent. showed varying amounts of carbon monoxide in the air. Ventilation was inadequate in all. Not one had a system of artificial ventilation. The following description is typical of the garages visited by Dr. Ciampolini:

> . . . . an old livery stable, of large dimensions, beneath a dwelling house, dark

and damp and irregular in construction. At about 8 A.M. the carbon monoxide content of the air, in one of the many corners, reached 0.2 per cent., and the blood of the proprietor, who "had not been feeling quite well for a long time," showed a carboxyhemoglobin saturation of 18 per cent. This particular garage had been storing heavy trucks for the night and it was almost empty at the time of the inspection, but carbon monoxide, although lighter than air, rises slowly and does not oxidize to carbon dioxide spontaneously.

Benzol Poisoning

Benzol (benzene) is the name of a poisonous liquid made from coal tar which has come into wide use in America since the war. This is because of its excellent mixing qualities and because it is cheap. Benzol (benzene) must not be confused with benzine, which is made from petroleum and which is not nearly so poisonous. Benzol is now being used in gasoline in many parts of the country. Analysis of a sample of this type of gasoline shows the following proportions (7).

	Per Cent.
Benzol	69.0
Toluol	15.5
Solvent naphtha	13.5
Heavy naphtha	2.0
Total	100.0

Lehmann found that 2 to 3 parts of benzol to 100,000 parts of air breathed for a few hours may cause loss of consciousness (8). Poisoning may be acute, resulting in hemorrhages and death, or it may be chronic—the result of absorbing small doses over a long period of time.

Chronic benzol poisoning is one of the hazards to which automobile mechanics are exposed. The worker rarely has any idea of what is troubling him. Headaches, nausea with vomiting, and finally bleeding under the skin mark the progress of the disease. Dizziness also appears early. Benzol is so destructive of life because it attacks the blood-making powers of the body. It destroys the red blood cells (the oxygen carriers of the body) and the white cells which protect the body against disease.

Benzol can be taken into the body through the skin, by dipping the hands in it, or its fumes can be breathed from the air. When "benzol gas" is used, benzol in amounts dangerous to health may be present in exhaust gas.

Protecting Garage Workers from Exhaust Gas

Exhaust gas is hot and therefore much lighter than ordinary air. If given a chance it will rise. All that is necessary is to send the gas upward. With the present horizontal exhaust used on automobiles this is impossible. The effect of the horizontal exhaust is to mix the gas almost immediately and completely with nearly the entire air of the garage. The following experiments were made by Prof. Yandell Henderson and Prof. Howard W. Haggard (1) in studying carbon monoxide poisoning at Yale University:

Test No. 1.—A truck was run idle for five minutes in a closed garage. A sample of air taken near the face of the observer (5 feet above the floor) contained 7.3 parts of carbon monoxide to 10,000 parts of air.

Studies for the vehicular tunnel now being built between New York and New Jersey place the safety limit of carbon monoxide in the air at 4 parts to 10,000 parts of air. This is for

persons sitting quietly in machines and exposed for only one hour. Men at work breathe in about three times more carbon monoxide in one hour than men at rest. For garages where there is exposure for several hours, 1 part of carbon monoxide to 10,000 parts of air (7, p. 138) is the largest amount workers can risk breathing. This is the amount arrived at by Dr. J. S. Haldane, the English authority, and adopted as the standard (7, p. 80). The air in the garage described above, therefore, contained more than seven times as much carbon monoxide as can be breathed with safety.

Test No. 2.—After the garage tested above had been aired, the same truck was run for the same length of time with the ventilator in the roof open. A sample of air at the same height from the floor contained 9.2 parts of carbon monoxide—more than eight times as much as can be breathed safely.

Ordinary methods of ventilation give garage workers no protection from the fumes contained in exhaust gas as long as motors are run with horizontal exhausts.

The Vertical Exhaust for Automobiles

One solution of the problem of getting rid of exhaust gas would be to send it up in the air toward the ceiling and then out through a ventilator. This method was tested in the same garage used in Tests 1 and 2 by equipping a truck with a vertical exhaust, consisting of a bent pipe attached to the present exhaust, carried up along the back of the car or truck to the top. When this type of exhaust was used tests of the air 5 feet from the floor, after the engine had been running ten minutes, and with the ventilator of the garage open and directly above the exhaust of the car, showed only 0.5 parts of carbon monoxide to 10,000 parts of air—a safe amount.

Treatment of Carbon Monoxide Poisoning

The common name for carbon monoxide poisoning is gassing—asphyxiation. If a man is removed at once from the poisonous atmosphere to fresh air, the carbon monoxide leaves the blood in a few hours. The quicker it is breathed out of the blood the better are the chances of recovery. If the gassing has not been too long or severe, and the first-aid treatment has been prompt and correct, the man will recover.

First-aid treatment for carbon monoxide poisoning may be carried on by workers. They must be trained to know what to do, for wrong methods may kill a man instead of saving him. It is possible and practical to work out a method for taking care of cases of gassing *in every shop*.

Other Hazards of the Trade

Gasoline Poisoning

The following facts in regard to gasoline poisoning are taken from personal communications from Professor Haggard (9):

Illness resulting from breathing the air in garages is frequently thought to be caused by gasoline. Gasoline vapors may be present in motor exhaust gas but there is never enough to be harmful. Exhaust gas is made poisonous by the carbon monoxide which it contains and also by benzol if it is present. Gasoline vapor has a characteristic smell, while carbon

monoxide is odorless. When a carburetor is set for a rich mixture and the exhaust smells of unburned gasoline, the carbon monoxide is increased and the gas becomes more poisonous to breathe because of the greater amount of carbon monoxide, not because of the gasoline.

Gasoline vapors are poisonous to breathe when present in the air in large quantities. Such high concentrations can arise under the following conditions:

1. When a large quantity of gasoline is spilled on the floor of a closed room or when a gasoline tank is drained into a pit in which a man is working. The vapors of gasoline are heavier than air and collect in low places.

2. When gasoline is used to wash an engine or parts in a poorly ventilated room. The danger is increased if the gasoline is sprayed on or if the engine is hot while being washed.

3. When gasoline leaks from storage into the underground pipe rooms of gasoline storage or dispensing stations. A very small leak in a cellar may build up a high concentration of gasoline because the vapors do not rise quickly.

Symptoms.—Men poisoned by gasoline become excited and dizzy and develop a "jag." If the poisoning is very severe, convulsions develop and are followed by unconsciousness. Fatal poisoning from gasoline vapors is rare. Men who frequently get their skin wet with gasoline may develop skin eruptions.

Treatment.—Gasoline poisoning is treated the same as carbon monoxide poisoning:

1. Remove the man to fresh air.

2. If breathing has stopped, give manual artificial respiration at once.

3. In every case the man should be given an inhalation of oxygen containing 5 per cent. of carbon dioxide continued for fifteen minutes or longer.

Prevention.—Poisonous amounts of gasoline need not be present in garages or repair shops. To prevent the accumulation of large amounts of gasoline vapors care should be taken to avoid spilling and leaks. Wherever gasoline is present in large amounts the danger from fire is very serious.

Gasoline should never be taken into or allowed to run into a pit which is to be used by a man. The pit method of repairing is a menace to health both from the standpoint of poisoning and as a fire hazard. It should not be tolerated.

Washing or spraying with gasoline should be done only out of doors.

Men should never enter underground pipe rooms which smell of gasoline or go into tanks which have contained gasoline unless carefully protected against the fumes, as there is danger of being overcome. The ordinary gas mask gives no protection against gasoline vapors. During such severe exposure unusual precautions must be taken. Professor Haggard recommends that a mask attached to a hose through which is supplied fresh air would offer protection.

Acetylene Welding

Acetylene welding should be carried on only when men are supplied with proper protective devices, and where the shop is equipped to prevent accidents.

Burning Oil (Acrolein)

Burning oil gives off a smoky substance, exceedingly irritating to the

nose, throat, and eyes. This substance is called acrolein. Since acrolein is much heavier than air, ordinary methods of ventilation will not remove the irritating fumes. All work on automobiles which is likely to produce smoke from burning oil should be done out of doors.

Accidents

Every garage and repair shop should be organized and equipped to prevent accidents.

Hours of Work

Hours of work bear a direct relation to the accident rate and the hazard of carbon monoxide poisoning. The longer a worker breathes in carbon monoxide fumes, the greater the danger. The reduction of working hours is, therefore, an essential factor in protecting the health of automobile mechanics.

Conclusions and Recommendations

The serious health hazards to which automobile mechanics are exposed call for the adoption of a national health program for the protection of workers in garages and repair shops. Such a program should include: control of poisons and other trade hazards; control of accidents; shop sanitation; and educational material for the membership.

This plan of health organization would serve as a basis for: negotiations with employers; introduction of city and state regulations; securing to members the benefits of compensation; and providing in every shop emergency treatment to prevent deaths from carbon monoxide poisoning.

For the development of such a program we recommend:

1. The assembling of first-hand evidence showing the actual physical condition of men exposed to trade hazards in garages and automobile repair shops.

No study of this kind has yet been made. The investigations so far conducted have dealt mainly with proving the presence of carbon monoxide in the air and in the blood. A thorough medical examination of at least 200 automobile mechanics at present employed in garages and repair shops would produce the facts required. Such examinations should be conducted under the auspices of the Union by a physician qualified to recognize occupational symptoms. Records of medical examinations should be confidential and the property of the Union—the findings to be used as scientific evidence through which to secure health regulations in the trade.

2. A study of all available information on accidents; causes of death; time lost through sickness; average length of time workers stay in the trade; and other related data.

3. A study of exhaust gases from various types of gasoline fuels to prove the nature and extent of poisons to which garage workers are exposed.

4. An educational campaign in every local union to acquaint the membership with the dangers to which they are exposed and the steps being taken by the Union to control these dangers.

5. The installation in every garage and repair shop of first-aid equipment of a scientifically approved type for supplying oxygen mixed with 5 per cent. of carbon dioxide (2).

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DETERMINATION OF SUSPENSOIDS BY ALTERNATING-CURRENT PRECIPITATORS*

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IN THE mining and metallurgical industries, numerous problems arise requiring determinations of solid and of liquid particles suspended in air. Frequently, these problems are of local interest and involve purely economic or operating difficulties; on the other hand, toxic effects from the inhalation or the ingestion of substances suspended in air may be a matter of concern. For checking up process improvements or for determining ventilation efficiencies in problems of this general nature, various methods have been proposed. Although simpler methods are often satisfactory, precipitation combines several desirable features that other methods lack. This paper is, therefore, devoted to a discussion of portable alternating-current precipitators applicable to the quantitative determination and microscopy of dusts, fumes, and smokes in air.

Small particles suspended in gases, such as air, are referred to in the literature as aerosols or suspensoids. Of these terms, suspensoids appears to be preferable as being more nearly in keeping with words in everyday use. In problems involving air pollution by small particles—by suspensoids—it is convenient to distinguish three broad classes based on the size, the degree of dispersion, and the method by which the particles become suspended in the air.

Dusts.—Particles or aggregates of particles, 150 to 1 micron in diameter, that are thrown into the air by mechanical agencies are termed dusts. Examples are silica, talc, cement, organic dusts such as hard rubber, starch, and cocoa; flocculated fume and smoke products.

Fumes.—Particles, 0.2 to 1 micron in diameter, formed from chemical or physicochemical reactions are known as fumes. Examples are ammonium chloride, lead and mercury, zinc and magnesium oxides, fogs, and acid mists.

Smokes.—Particles, less than 0.3 micron in diameter, formed by incomplete combustion of carbonaceous and other substances are called smokes. Examples are the particles formed from burning tobacco, oil, tar, and gas.

These classes resemble those originally suggested by Gibbs (1), except that dusts cover a wider range of particle size and the size limitations for fumes and smokes overlap. In

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spite of obvious errors resulting from the inadequacies of classification, several features differentiating the three groups can be distinguished. Uniformity in the size of the particles and the tendency to flocculate or aggregate in air increase as the particles become smaller. Under still-air conditions and normal temperatures, dusts settle out with acceleration and do not diffuse. Fumes settle at rates approximating those predicted by Stokes' law and diffuse to some extent; while smokes diffuse, show Brownian movement, and settle so slowly that their settling rates, even in still air, may be ignored unless the particles become united into larger aggregates.

In establishing the principles and the practical operating details of his process, Cottrell was concerned, in his original work, with large installations. No attempt seems to have been made to develop small portable precipitators until Tolman, Reyerson, Brooks, and Smyth (2), in 1919, described a suitable equipment. By means of high-tension current, rectified by a kenotron, particles were precipitated on a thin aluminium foil and the increase in weight of the foil determined. Somewhat later, Bill (3) published an account of dust determinations obtained with a small electric precipitator that differed from Tolman's in the use of a mechanical stick rectifier instead of a kenotron. At about the same time, Lamb, Wendt, and Wilson (4) described an electric fume or smoke mask in which a storage battery and an induction coil served as the source of high-tension current. These authors used glass tubes wrapped with metal foil for collecting electrodes; the precipitating electrodes were made to bristle with sharp points protruding radially. Several of these tubes were placed together in a bundle with the connections for air flow and current in parallel. Although no rectifying device was utilized, the fact that this method, if glass tubes were used, could produce complete precipitation without complete rectification does not seem to have been considered. Strong (5) has obtained a patent for a small precipitator much like Lamb's, but in which only one tube is used. Lamb suggested using several tubes connected in parallel, although his quantitative data were obtained with but one tube.

For studying the effects of covering the precipitating electrodes with glass tubes, Shibusawa and Niwa (6) used a small precipitator with a kenotron and a glass tube wrapped outside with metal foil. Like Tolman, they obtained the high-tension current from a transformer. By means of oscillograms, they showed the characteristics of the voltage and current curves obtained when the precipitating electrode was positive, negative, and when alternating current was used and no kenotron was in the circuit. No experimental precipitations were made, however, with alternating current.

Katz, Longfellow, and Fieldner (7) (8) used a small precipitator, like Tolman's, but obtained unsatisfactory results. Drinker, Thomson, and Fitchet (9) used successfully a small portable precipitator having a glass tube, in which the current was supplied by a transformer, but in which no rectifier was used. Baumberger (10) and Salmang (11) both obtained satisfactory results with small rectified-

current precipitators for analyses of smokes. Warren and Read (12) experienced trouble with the precipitation method for dusts, while Weber (13) has recently shown the usefulness of a device, like Strong's, for determining acid mists.

If the apparatus for this general type of work is to be portable, it must be of reasonable weight. To some, a portable apparatus implies a device that can be carried in one's pocket; to others, it means an apparatus the size of the Orsat for gas analyses; still others are willing to use an equipment weighing 50 pounds or more, particularly if two observers work together. While no one would care to carry a 50-pound apparatus into an inaccessible place in a mine, it may be perfectly satisfactory for work in a factory where current is available. Where current is not available, the lighter storage-battery outfits can be used and determinations made without the use of any current other than that from the battery.

Alternating-Current Method of Precipitating Suspensoids

There appears to be a general misunderstanding of the difference between the alternating and the rectified-current methods of precipitating suspensoids, and an apparent reluctance to admit that efficient precipitation with alternating current is possible. The alternating-current method seems, perhaps, at first sight, to contradict the popular theory of rectified-current precipitation as originally described by Cottrell, Lodge, Walker, and others, and long since proved to be of great usefulness.

It will be recalled that Cottrell's original plant was built for the recovery of sulphuric acid mist—a conducting suspensoid. Small precipitators, like Tolman's, adapted directly from the Cottrell process, have been uniformly reported as successful, provided the suspensoid under determination was conducting. When this was not the case, as in the work of such careful investigators as Katz, Longfellow, and Fieldner, or Warren and Read, the results were not so good.

Frequent accounts are given of troubles in rectified-current plants operating on the original Cottrell principle. Often these troubles have been caused by dry nonconducting suspensoids, such as zinc oxide fume, which pile up on the collecting electrode and materially affect efficient precipitation. To remedy such troubles, the fume is humidified, and this renders the particles conducting.

For small precipitators, the alternating-current method, operating on what Strong (14) calls the condensed-field principle, avoids many, but by no means all, of these troubles and is especially suited to our problems because rectifiers are omitted. Rectifiers, whether of the mechanical or the thermionic type, like the kenotron, are troublesome and expensive and it is best to adopt a method that does not require their use. It should not be inferred from this that the rectified-current method is not adapted to small precipitators intended for long protracted runs on conducting suspensoids, such as acid mists. Their possible usefulness for such purposes is well demonstrated by the numerous Cottrell plants now working at high efficiencies and has been clearly shown

by Baumberger, Salmang, Shibusawa, and Tolman. In discussing the use of small precipitators, like Strong's, for determining acid mists (conducting suspensoids) Weber lays much emphasis on the need of adjusting the vibrator in the induction coil, a manipulation by which Lamb, Wendt, and Wilson found they could increase the positive part of the high-tension discharge and thus more nearly approach the rectified or unidirectional current discharge given by a method such as the transformer and kenotron. Weber reports having found the authors' (15) pyrex glass tubes "absolutely useless" at the low voltages he employed and used instead thin lead-glass tubes, thus again more nearly approaching the rectified-current precipitators. That Lamb and his associates or Weber either required or obtained the degree of rectification given by the kenotron has not been demonstrated.

It is our experience that, in small precipitators intended for runs of short duration, the alternating-current method can be used for both conducting and nonconducting suspensoids. For both long and short runs on nonconducting suspensoids, the alternating-current method, which utilizes the condensed-field principle, is much to be preferred. These facts, which can be very easily confirmed by anyone interested, were established some years ago, especially by the work of Strong to which reference has already been made. The authors' contribution to the use of small precipitators consists simply in adapting proved methods to the solution of their own problems and particularly to the use of the precipitation method for suspensoids to be examined under the microscope.

Constructional Details of Precipitators

The constructional details of small alternating-current condensed-field precipitators, whether of the storage-battery or the transformer type, are very similar. These precipitators consist essentially of a suitable device for obtaining high-tension alternating current, a collecting or "passive" electrode, a precipitating or "active" electrode, a suitable device for drawing the air through the precipitator, and a meter for measuring the rate of flow. A rheostat in the primary circuit is advisable, while a ground from the collecting electrode may be used but is not always necessary.

The Collecting Electrode

As shown in Figures 1, 2, and 3, the collecting electrodes are made of transparent dielectric substances, like quartz or glass, wrapped with a metal foil, such as aluminium. Although we have had no occasion to use electrodes other than glass or quartz, materials such as hard rubber, mica, or bakelite would probably work satisfactorily. While slightly better results are obtained with clear quartz tubes than with glass, they are much too expensive for general use. Ordinary lime-glass tubes are satisfactory for the very small precipitators, particularly if the suspensoid under determination is dry and nonconducting. For the larger precipitators, pyrex is preferred because it possesses higher dielectric strength than lime glass and is much less apt to be punctured should disruptive discharges take place. For determining acid mists, which are conductors, Weber, as has already been pointed out, considers pyrex "ab-

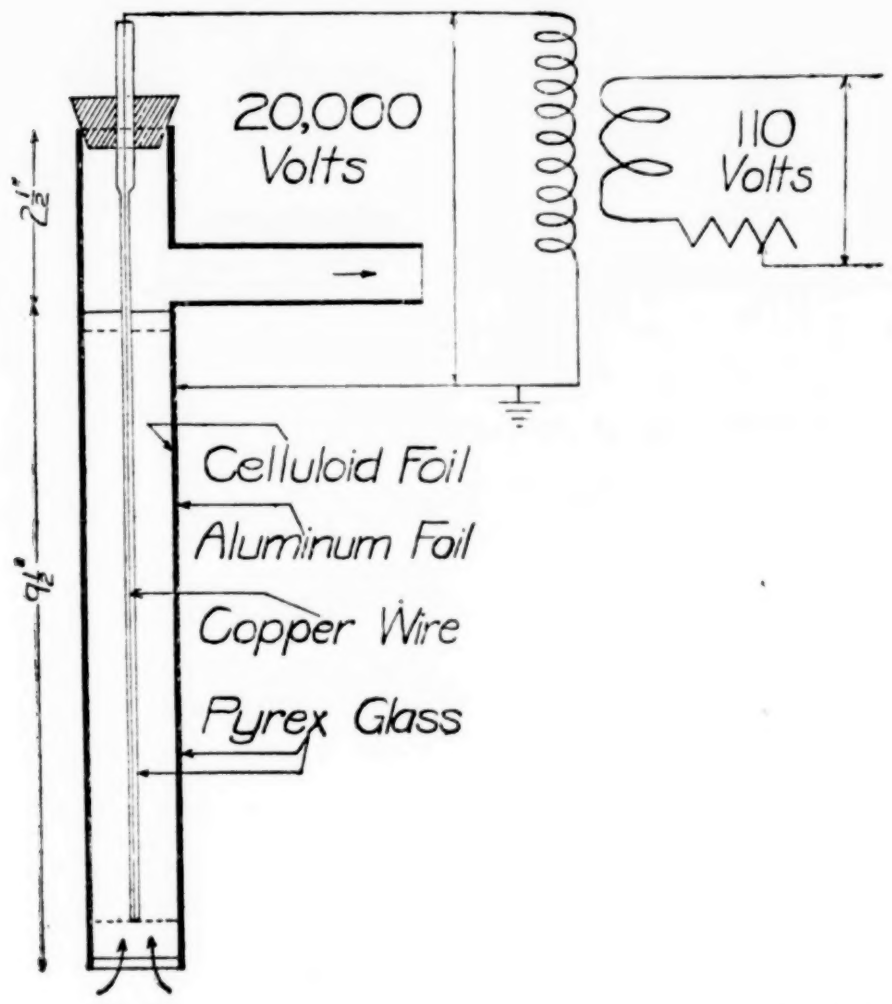

FIG. 1.—Transformer type of precipitator showing position of celluloid foil (solid line across tube) and metal foil (dotted line). Courtesy of the Journal of the American Society of Heating and Ventilating Engineers.

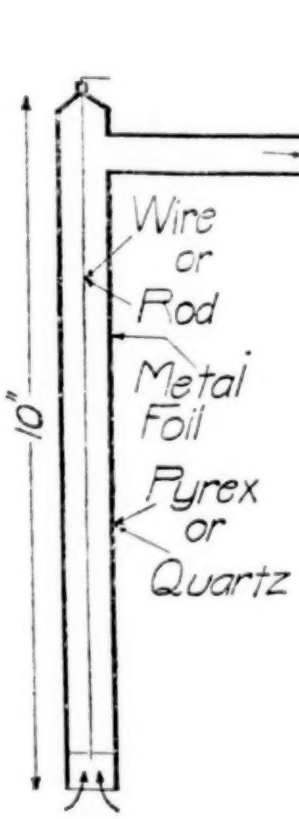

FIG. 2

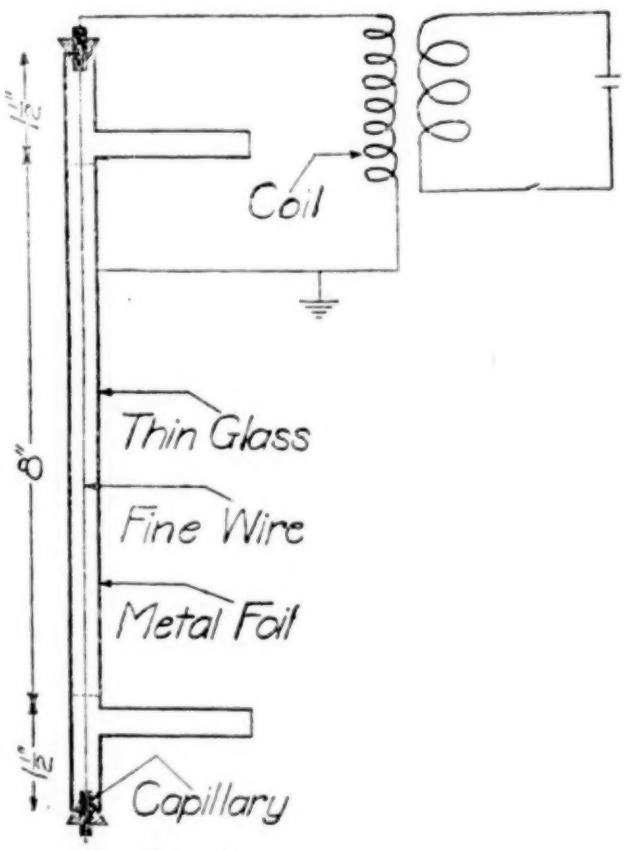

FIG. 3

FIG. 2.—Special collecting tube using no rubber stopper.
FIG. 3.—Battery type of precipitator for determining dusts.

solutely useless" and uses lead glass. With dry, nonconducting substances, we find lime glass superior to lead glass.

In both the small and the large precipitators, the optimum diameter of the tube is not sharply defined. There is always a fairly definite sized diameter which should not be exceeded; if smaller diameters are used, there seems to be little change in the efficiency of precipitation. For nonconducting suspensoids, like dry dust or fume, it is best to keep the diameter of the tubes small; for precipitating conducting suspensoids, the diameter of the tube should be made larger, otherwise sparking occurs and the efficiency of precipitation is reduced. For acid-mist determinations, Weber suggests paraffining the inside of the tube so that the accumulated drops run into a glass beaker beneath.

For convenience in handling the precipitate in the laboratory, it is advisable to make the tubes short. Very little advantage is gained by using tubes of lengths comparable to those used in the large-scale rectified-current plants. On the contrary, they are troublesome to clean and are, therefore, a drawback.

The optimum thickness of the walls of the tubes is also questionable and seems to vary roughly with the voltage applied and the dielectric strength of the material used. In the small precipitators, it is best to use thin-walled tubes; while in the transformer type of precipitator, tubes thick enough to obviate chances of puncturing are essential. In any case, there is no trouble caused by slight variations in either the diameter or the thickness of the walls of the glass tubes.

Use of Celluloid Foil for Collecting Precipitates

If efficient precipitation has been obtained in small units of either the direct or the alternating-current type, the precipitate is confined to a dense area beginning with the region of the electric field and extending upward but a very short distance. If precipitation has been incomplete, particles extend to the top of the tube. By catching the particles on aluminium foil instead of on the walls of metal tubes, Tolman found that the effectiveness of precipitation could be judged by observing whether or not the precipitate was confined to this dense area at the beginning of the foil. For our purposes, it is better to use transparent foils of low conducting power, such as mica or celluloid, than opaque metal foils like aluminium, although the latter are more satisfactory to weigh.[1] After a run has been completed, the effectiveness of precipitation can be judged by holding the transparent foil to the light and observing how far up the foil the precipitate extends. It is never necessary to run at such low voltages or such high air velocities that the precipitate extends to the top of the foil. For testing filtration efficiencies of fabrics, masks, or respirators the celluloid-foil method is especially useful and can readily detect minute amounts of fine fume particles by obtaining their accumulated precipitate over ten or twenty-minute periods.

[1] Contrary to our first impressions, the use of metal foil on both sides of the walls of the glass tubes gives poor recoveries in the alternating-current precipitators.

For the small precipitators, we have been unable to obtain celluloid foil thin enough to fit snugly against the walls of the tubes. Unless the foil fits tightly, precipitation is irregular and often inefficient. With the small precipitator, therefore, efficiency must be judged by the evidences of precipitation at the top of the tube or by the Tyndall effect in the air escaping from the precipitator.

Precipitating Electrode

As in the rectified-current method, the precipitating electrode should be centrally aligned and held rigid; otherwise the area covered by the precipitate is irregular and the precipitation efficiency may be low. In general, better results are obtained when the wire is fine, but it is unnecessary either to thread it, as Tolman did in his rectified-current precipitator, or to use Lamb's electrode with points protruding radially. The wire is enclosed in glass (Fig. 1) in order to hold it in rigid central alignment, to permit the use of copper instead of platinum, and to facilitate the withdrawal of the celluloid foil without disturbing the precipitate. Where the celluloid foil is not used, it is better to use tubes with two side arms (Fig. 3) for the entrance and escape of the air and to hold the wire in central alignment by capillaries inserted in rubber stoppers at each end of the tube. In larger units, like that shown in Figure 1, there is more than ample capacity, so that it is possible to use the method shown instead of the bare wire, although the latter is the more effective. In the case of the small precipitators, bare wires are advisable because the rate of air flow through the device, at best, is low.

No matter how fine the precipitating wire is made, traces of precipitate are obtained upon it in amounts that vary roughly with its diameter. Often the amount is small enough to ignore, particularly if the sample is taken for microscopic examination and is not to be estimated chemically or gravimetrically. In any case, the removal of these slight amounts is not difficult with either the enclosed or the bare-wire method.

Figure 2 represents one of the rather surprising liberties that may be taken with the electrical connections in precipitators for determining nonconducting suspensoids. The precipitating electrode, a fine stiff rod or wire, is fixed in the glass holder at the bottom of the tube, and is held by the constriction in the glass tube at the top. In spite of the contact between the glass holder fused across the tube and both the precipitating and the collecting electrodes, this type of tube is satisfactory both for the transformer and for the battery type of precipitator.

Suction Fan and Air Meter

An advantage of the precipitation over other methods for suspensoid determinations is the low resistance of the glass tubes to air flow, thus permitting the use of small motors for running the suction fan. For the transformer type of precipitator, a small 110-volt sewing-machine motor may be used, while small motors, run from the batteries, suffice for the smaller precipitators. For use in mines where compressed air is available and current is not, Warren and

Read suggest a compressed-air ejector as a source of suction for sampling dusty air.

Whether suction fans or ejectors are used, the rate of air flow is conveniently measured by a device such as the orifice meter or a glass resistance-flow meter. In all cases, the rates of flow can be controlled by rheostats on the motors, by bypasses, or by clamps on the rubber tubing connecting the various parts of the apparatus.

Permissible Rates of Air Flow

As in large plants, it is a simple matter to run the air through the precipitators too fast to catch all the particles. Running the air through too fast, or "overloading," can be detected by the methods already discussed and, in properly made tubes, can be avoided by increasing the intensity of the field or by lowering the rate of air flow, or by both. It is unnecessary to run the precipitators at such high rates that particles escape precipitation.

On the transformer type of precipitator, rates of air flow varying from about 5 to 50 liters a minute are the most convenient. The bulk weight of the apparatus depends mainly on the transformer and varies, in our apparatus, from 25 to 50 pounds. With the lighter types of transformer now available, this weight could doubtless be much reduced. When storage batteries are used, the weight can be reduced to but a few pounds, while the rate of sampling is correspondingly reduced (see Fig. 4). With our apparatus, the storage-battery method permits rates of about 2 to 8 liters a minute. Strong states that very small precipitators, run from dry batteries, can now be obtained for $8.00.

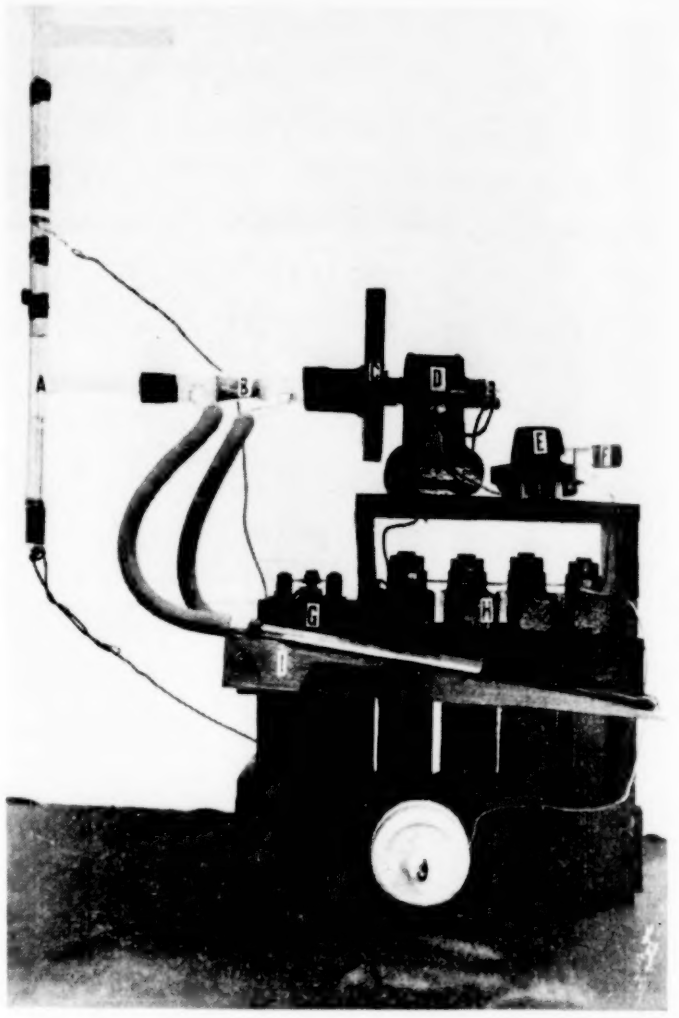

Fig. 4.—Portable storage-battery type of precipitator for determining dusts in air, weighing 13 pounds.

A—Precipitator tube of lime glass. (See Fig. 3.)
B—Glass flow meter.
C—Suction fan.
D—Portor motor, K & D, No. 1.
E—Rheostat for controlling speed of motor.
F—Switch for motor circuit.
G—Ford induction coil.
H—Four Edison alkali batteries, type L-20.
I—Inclined manometer, using ether, for registering pressures on flow meter.
J—Switch on primary of Ford coil.
(Note that precipitator tube needs no support other than rubber stopper at exhaust of tube and stiff high-tension wires to Ford coil.)

Accuracy Attainable by the Alternating-Current Method

As pointed out, the alternating-current method of precipitation permits recoveries at efficiencies very close to 100 per cent. Whether the rate of

air flow through the apparatus should be measured with a comparable degree of precision, depends on the problem in question. It is difficult, with pitot tubes, orifice meters, and similar devices, to measure rates of air flow to an accuracy greater than 95 per cent., and dry or wet gas meters are too bulky for convenient use in any but laboratory work. Small electric meters, such as are now available for measuring gas concentrations in chimneys and in alveolar air, could doubtless be applied to precipitators. As the accuracy attainable by the precipitation method is dependent on the measurement of air flow through the precipitator as well as on the efficiency of precipitation, the individual investigator must choose his method of metering the air in accordance with the precision his problem requires.

Application of Precipitation to Microscopy

By using the celluloid foil, samples may be obtained in a state convenient for mounting and examining under the microscope. Strips are cut from representative portions of the foil and are mounted on glass slides by means of a few drops of amyl acetate. Warming the slide at a gentle heat causes the foil to lie flat against the glass and eliminates surface irregularities.

As the particles are driven into the celluloid with considerable force, it is usually possible to add a drop of oil for examination under an oil immersion lens without disturbing the particles. With many substances, particularly dusts, permanent mounts can be made by fixing the celluloid on the glass slide with the precipitate next the glass. It is often convenient, when using the celluloid-foil method, to withdraw the foil after precipitation and to place it and the precipitating electrode in a glass tube of the same diameter as the pyrex tubes. Packed in this way, the samples can be transported or mailed without disturbing the precipitate, and slides may be prepared several months after the samples are taken.

Size Distribution of Particles in Precipitate

One of the main advantages we have hoped to obtain by this method is the precipitation of particles in the state in which they occur in air; for example, if the particles were originally flocculated into aggregates, to show them as aggregates, and if dispersed, to obtain them in the same way on the celluloid foils.

We have shown elsewhere (9) that, with the alternating-current method, dust or flocculated fume particles can be caught at higher rates of air flow than dispersed fumes, while smokes are still more difficult to collect—an effect due probably to the number or concentration of the particles and not to any inherent properties of these different substances. This indicates that the smaller the particles the more difficult they are to precipitate, and suggests the possibility that small particles might be precipitated farther up the tubes than large particles. As a matter of fact, however, in complete precipitation of nonuniform substances, such as dust, the precipitate is confined to such a small area that this size distribution is not noticed. As yet, we have obtained insufficient evidence to settle the question one way or the other. It is a matter of interest

that Rohmann (16) has found a method of measuring size distribution by utilizing the precipitation principle but employing low voltages. The dispersed cloud is passed through a direct-current field and the distance the particles travel before precipitating gives an index of their size.

From the literature on the rectified-current process, one might infer that the alternating-current method would produce mainly flocculation. While such an effect can be shown in a large container filled with a smoke, fume, or dust, conditions in the precipitator are quite different. The time for the particles to pass through the tubes is much too short for them to be caught simply as a result of flocculation. No such effects, moreover, are apparent on microscopic examinations of dry substances precipitated on the foils.

Objections to Precipitation Method

In the transformer type of precipitator, voltages varying from 5,000 to 20,000 are used, depending on the suspensoid under investigation. In storage-battery precipitators, the voltage varies from about 1,000 to 5,000 according to the number of batteries used. The danger from shocks in the transformer precipitators is unquestionably real and not to be dismissed casually. Shocks from the battery type of precipitator are about like those that one gets from the spark plug of an automobile—very unpleasant, but not serious. We have used both types of precipitators constantly during the last three years in both laboratory and field work and see no reason why the voltages employed offer any practical difficulties.

The fact that celluloid foil can be used in the collecting tubes shows that sparking troubles are few, but they do occur occasionally, particularly with wet conducting substances like tobacco smoke.

The fire or explosion hazards in small precipitators for dusts like flour, cocoa, hard rubber, bituminous coal, zinc powder, and sulphur are questionable. To render inflammable an air mixture of these dusts has been shown by Trostel and Frevert (17) to require extremely high concentrations—concentrations too great to maintain more than momentarily. Consequently it is difficult or impossible to suspend inflammable concentrations of these dusts in air long enough to pass them through the precipitators. In experimental work no trouble has been experienced from the substances named; we would, nevertheless, consider it a needless hazard to use the precipitators in atmospheres where there was the slightest possibility of encountering dangerous dust-air mixtures.

With gases like carbon monoxide, hydrogen sulphide, or vapors from alcohol and ether we have obtained mild explosions in the precipitators. Inflammable gases or readily oxidizable suspensoids should be handled with caution in precipitators of any size, and experiments should first be made in small apparatus at low voltages giving but little ozone and feeble coronas.

Summary

The constructional details and adaptation of portable alternating-current precipitators to the quantitative determination of suspensoids such

as dusts, fumes, and smokes are discussed. The distinction between the alternating-current method, using glass collecting electrodes, and the rectified-current method, using metal collecting electrodes (Cottrell process) is brought out. Poor results obtained in the past with small precipitators are attributed to failure to distinguish between conducting and nonconducting dusts, fumes, and smokes. A portable storage-battery induction coil type of precipitator weighing 13 pounds is described and illustrated. For taking samples for miscrosopic study, the author's method of inserting a celluloid foil in the collecting electrode and catching the precipitate upon it is described. These foils or the entire collecting electrode can be mailed or transported without danger of disturbing the precipitate and representative slides can be made up later in the laboratory.

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THE DETERMINATION OF SMALL AMOUNTS OF ZINC IN MATERIALS OF ORGANIC NATURE: A MICROCHEMICAL METHOD BASED ON THE FLUORESCENCE OF ZINC SALTS WITH UROBILIN*

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I. INTRODUCTION

A NEW method of determining minute amounts of zinc quantitatively has been developed, based on the known property of zinc salts of fluorescing when allowed to react with urobilin or stercobilin; and this method has been adapted to carrying on an effective study of the normal and abnormal occurrence of zinc in vegetable and animal materials where the amounts of the samples are small, and where the content of zinc in the sample to be tested is of the order of 0.005 to 0.5 mg. Methods have been developed to determine zinc in amounts greater than 0.1 to 1 mg. but no method as discussed in the literature was found to be suitable for quantitative work where zinc ranged in amounts below this. In a study of the hygiene of zinc it is necessary to determine the zinc content of various foods, animal tissues and bone, and excreta, in cases of both normal and abnormal contact with zinc. Often only small amounts of samples are available, as, for instance, in the determination of the zinc content of the various organs of the rat where the organic material to be analyzed weighs between 0.5 and 10 gm.

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II. AVAILABLE METHODS FOR THE DETERMINATION OF ZINC

The determination of zinc where the sample of material to be analyzed is unlimited, or where the zinc content is high, may be carried out by several gravimetric and volumetric methods (1). Where the amount of zinc being determined is as low as 0.5 to 5 mg., the turbidimetric methods employing ammonium sulphide (2) or potassium ferrocyanide (3) may be used. For the determination of amounts of zinc below 0.1 mg. several colorimetric methods have been proposed. One such method (4) is based on the blue color obtained when a solution of zinc is treated with an ammoniacal solution of resorcin, the amount of zinc being estimated by the intensity of color as measured in a Duboscq colorimeter. While the accuracy claimed for the method was of the order desired for the purposes of a research on the hygiene

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of zinc,[1] the method was found to be subject to uncertainty and irregularity, and no consistent results were obtained with it. A method for the detection of zinc by means of potassium cobaltocyanide (5) was considered without success in an attempt to apply it quantitatively.

The formation of lakes with zinc salts and certain dyes seemed to offer a possibility for a microtitration method applicable in the determination of small amounts (6), and was investigated carefully in the most promising cases. The method was applied by Brenner to the determination of cobalt by means of nitroso-chromotropic acid, by titrating a solution of cobalt with a standard solution (2 moles) of the dye. He was able to get an end point at the color change when an excess of the dye was added (the end point was determined by comparison with a standard end point). The action of various metals on several dyes was mentioned and the color changes were tabulated, including those changes brought about by zinc salts. The general suggestion was made that these color changes might be used in a quantitative microtitration method similar to that described in detail for cobalt and copper.

I carried out experiments using several dyes, and found that National Superchrome black 13 N[2] (Schulz No. 184) when in dilute, ammoniacal solution reacted quantitatively with small amounts of zinc (as low as 0.001 mg.) with a color change from blue to red. Several other dyes gave similar color changes, although the reactions were not so sensitive as in the case I have cited. The method is not accurate; furthermore, the reaction is not specific for zinc, since other metals, especially calcium and magnesium, give similar color changes in every case. It was found to be extremely difficult, if not impossible, in the most simple procedures for the isolation of the zinc salt, to free the solution from traces of calcium and magnesium, and therefore the method was abandoned as impractical.

In the color reactions involving zinc, which have been discussed so far, the element itself is not responsible for the color,[3] as is the case with many colored compounds of copper and nickel (*i.e.*, the molecular compounds of nickel with di-methyl-glyoxime and di-thio-oxalic acid). Zinc imparts no color to its compounds; furthermore, although it has a modifying effect on the color produced by certain groups (*i.e.*, dyes and complex cyanides), the color itself is due primarily to the group associated with the zinc atom. For the purposes of an analytic method these modifying effects of zinc on various colored groups are of small value because of the similar and often greater effects of other metals, and the difficulty in completely removing them.

III. The Development of a New Microchemical Method for the Quantitative Determination of Zinc

A. Urobilin and its Reactions.—The well-known reaction of zinc salts with

[1] I refer here to the research on the hygiene of zinc that is being carried on at the Harvard School of Public Health, by Dr. C. K. Drinker and others.

[2] Supplied by the National Aniline & Chemical Company.

[3] The reactions with resorcin and urobilin may possibly be exceptions, although the chemistry involved is not at all clear.

urobilin or stercobilin (organic substances of unknown structures) to form a highly fluorescing substance in weakly alkaline, alcoholic solution is a specific reaction for zinc. This reaction is apparently an exception to the foregoing generalization in regard to the relation of color to the zinc atom, for this green fluorescence is a specific property of zinc alone, and no similar or parallel effect is produced by any other metal. Here, however, the chemistry of the reaction is not clear and therefore no definite statement concerning the relation of the zinc to color can be made. The work of several authors (7) has shown that the minute amounts of zinc dissolved from galvanized containers by commercial alcohols, which are often faintly acidic, may be tested for by means of a dilute solution of urobilin. They obtained an appreciable fluorescence in those cases where there was contamination by zinc. Because the reaction is specific and extremely delicate, I have studied it further and have developed and applied the test to the quantitative estimation of minute amounts of zinc.

Urobilin, a pigment found in bile, in the urine in certain diseases, and in normal urine (in the form of its chromogen, urobilinogen), was isolated by Jaffe (8), who prepared the substance in a high state of purity. He discovered its remarkable property of giving strongly fluorescing solutions with zinc salts. Many investigators have studied this substance and a variety of views concerning its nature and origin are prevalent. Probably because of the difficulties of purifying the substance, the samples obtained from various sources (including the substance stercobilin, obtained from the feces (9)) vary in properties and in analysis, and therefore the identity (10) of these various substances is not established, although an affirmative view on the question is held by Garrod and Hopkins on the basis of their work on the optical properties. The power of fluorescing with zinc salts varies somewhat but is identical in character in samples obtained from various sources. Since the pigments from whatever source agree in their principal chemical properties, I shall assume, in agreement with Garrod and Hopkins, that they are identical. The substance stercobilin, obtained from the feces, is the easiest to obtain and was used throughout this research, and in referring to it I shall use the term urobilin in accord with the name used to describe the original substance isolated from urine by Jaffe.

The structure of urobilin is not known. There is evidence that it contains a pyrrol group (11). It is quite soluble in alkalies and much less so in acids. Ammonium sulphate is a specific precipitant for urobilin, and in a saturated solution the pigment is quite insoluble, although soluble in pure water and ammonium chloride solution. The substance is obtained usually as a brown solid, and is soluble in most organic solvents, but is insoluble in petroleum ether and ligroin. Certain metal hydroxides carry down urobilin, and zinc and lead have been used for this purpose in several methods of preparation. The few facts I have enumerated throw but little light on the nature of urobilin.

B. Preparation of Urobilin.—The methods of preparation of urobilin from urine do not yield products of

uniform purity. The original method of Jaffe (8) yielded a very pure product. In the main the method involved precipitating the phosphates with ammonia, and then carrying down the urobilin by means of zinc hydroxide. Méhu (12) devised a method based on the insolubility of urobilin in saturated ammonium sulphate solution which had been slightly acidified. Garrod and Hopkins (10) modified the method by first saturating with ammonium chloride, in order to precipitate the urates, a purer product being the result. Several investigators used extraction processes, with chloroform or a chloroform-ether mixture (7). The urine was first acidified to aid in extraction. Urine is a poor source of urobilin, however, since all of the methods yield only very small amounts of the pigment. Mention should be made at this point of "hydrobilirubin," prepared from bilirubin by reduction with sodium amalgam (13), for the product resembles and in all probability is identical with urobilin or its chromogen. Urobilin was obtained in better yields from normal feces (this is the so-called stercobilin of Vanlair and Masius (9)), and a method has been described by Auché (14) which involves extraction with chloroform, evaporation, oxidation of the chromogen in the air, and treatment of the residue with ligroin to dissolve out impurities. Purification was accomplished by extracting the urobilin with water, and precipitating with zinc hydroxide. An adaptation of this method was used in this research and will be described briefly.

Fifteen hundred grams of normal feces were placed in a large Erlenmeyer flask and treated with about twice the volume of chloroform, the mass being shaken from time to time for several hours. The chloroform was decanted, and a second portion was added and shaken occasionally for ten to fifteen minutes and decanted. The mass of feces was extracted three to four more times and the residue containing a large amount of emulsified chloroform was discarded. The chloroform was distilled off and the black, tarry residue was allowed to stand in contact with air in an open dish for several days. On treating the black mass with petroleum ether, a brown precipitate was formed and the black oil passed into solution. On filtration and repeated washing with petroleum ether, a brown powder was obtained and the filtrate was discarded although it contained appreciable amounts of urobilin, dissolved through the influence of the greases present. Urobilin is insoluble in pure petroleum ether. The brown powder was dissolved in chloroform and reprecipitated by diluting with petroleum ether, a brown, crystalline solid being obtained. The substance was reasonably pure as is shown by the fact that it dissolved to give a clear solution, yellow in ammonia and pink in acid; and that with zinc salts (ammoniacal) it gave a clear pink solution with a strong green fluorescence. The yield was 1.5 gm. The product was of ample purity for the purposes of this research.

C. The Estimation of Zinc with Urobilin.—When a small amount (0.1 mg.) of zinc acetate is added to an alcoholic ammoniacal solution of a trace of urobilin, an immediate, intense green fluorescence develops

which is stable for several weeks. When the test is made with very small amounts of zinc (using 50-c.c. Nessler tubes), 0.001 mg. gives a noticeable greenish fluorescence which is not visible in ordinary light but which is readily apparent under a strong arc light with an ultraviolet filter, or when illuminated by a carbon arc lamp, the bottom of the tube being protected from reflected light, and the observations made in a dark room. With a carbon arc lamp and an ultraviolet filter, amounts of zinc as low as 0.0001 mg. can be detected by the fluorescence. The quantitative estimation of zinc using the ultraviolet filter was not adaptable to working on a scale as low as this for many reasons, including the difficulties in preventing contamination by zinc and of obtaining distinct differences of intensity of fluorescence in the Nessler tubes.

When solutions were made up with varying amounts of zinc and viewed under the carbon arc lamp without an ultraviolet filter, an excellent gradation of intensities was obtained between 0.001 and 0.01 mg. of zinc, and it was found possible to distinguish differences of concentration of 0.00025 to 0.0005 mg. When the zinc concentration was below 0.001 the color was barely discernible, and when over 0.01 mg. the fluorescence was so strong that the difference between 0.01 and 0.015 mg. was hardly noticeable. Thus a definite range of concentration was found to which the sample to be tested must be diluted in order to make a quantitative determination.

Since it is possible to estimate within this range (0.001 to 0.01 mg.) differences of concentrations of 0.0005 mg. to 0.00025 mg., the accuracy of the determinations (at a concentration of 0.004 mg. of zinc where conditions are at their best) is one part in eight to sixteen, or roughly 10 per cent.

D. Interference with Fluorescence.—The accuracy and delicacy of the test was affected by many factors, and I shall briefly consider them. The fluorescence with amounts of zinc as low as 0.005 mg. was destroyed in the presence of many substances, and the permanence of the color was affected by impurities present in the reagents or the solvent. Commercial 95 per cent. ethyl alcohol was used as the solvent. In order to remove impurities that imparted a yellow color to alkaline solutions, it was distilled over lime. Recovered alcohol was found to accumulate impurities (probably aldehydes) which caused the fluorescence with urobilin and zinc salts to fade appreciably in a short time, thus making consistent readings difficult or impossible. Careful purification of recovered alcohol by repeated distillation was found to be essential in order to obtain consistent results.

A large excess of ammonia or ammonium salts was found to have a decided depreciatory effect on the fluorescence. In a typical test as described with 0.005 mg. of zinc in a 50-c.c. Nessler tube, 6 drops of concentrated ammonia had practically no effect but 12 drops caused a very marked decrease in the intensity of color.

An excess of urobilin diminished the sensitivity of the test owing to the high coloring power of the pigment itself. A standard solution of urobilin was prepared to contain approximately enough pigment per cubic centimeter to react quantitatively with 0.015 mg.

of zinc. The reaction between an ammoniacal solution of urobilin (yellow in color) and zinc was said to be complete when the yellow color was just destroyed by the zinc salt with the formation of the characteristic pink color (by transmitted light) of the zinc compound. By using the same amount of urobilin in every experiment, accurate comparisons of unknown samples could be made with samples containing known amounts of zinc.

The test with urobilin was tried with the metals which were likely to occur with zinc during a typical analysis, and no metal was found which would react to give a fluorescence of itself. It was found, however, that small amounts of many metal salts interfered seriously with the test for zinc, apparently through the formation of a more or less stable, nonfluorescing compound with urobilin itself.

The metals studied quantitatively are listed in Table 1, where the effect of various concentrations of the metal on a typical test for 0.004 mg. of zinc are given. Copper has the greatest effect, and calcium and magnesium very marked effects. The alkali metals, sodium and potassium, in small amounts also interfered with the test. It should be observed that these metals must be present in quantities approximately equal to, or greater than, the amount of zinc, before appreciable effect is noticed; and, therefore, if the zinc sample to be tested contains less than 20 to 30 per cent. of other metal salts, no interference will arise. The effect of cadmium on the test was, curiously enough, the reverse of that of the metals listed in Table 1, whereas by itself it gives no fluorescence with urobilin. The test with 0.004 mg. of zinc is increased slightly when 0.005 mg. of cadmium is present, is increased quite appreciably in the presence of 0.01 mg., and is nearly doubled with 0.02 to 0.03 mg.

TABLE 1.—THE EFFECT OF VARIOUS AMOUNTS OF CERTAIN METALS ON THE INTENSITY OF FLUORESCENCE WITH 0.004 MG. OF ZINC

METAL	THE AMOUNT OF METAL IN MILLIGRAMS PRODUCING				
	No Change	Slight Decrease	Appreciable Decrease	Decrease to One-Half	Almost or Complete Extinction
Ca	0.002	0.006	0.012	.....	0.040
Mg	.002	....	.006	0.012	....
Ni	.001	.005	.010	.020	.050
Co	.002	.010	....	.040	....
Mn	.006	.040	....	....	....
Cu	.001	.005	....	....	.010

The procedure for preparing a sample of zinc for analysis by the reaction with urobilin, on the basis of the facts outlined above, then, must involve a separation of zinc from practically all other substances, and required the development of a special technic which will be discussed at length.

IV. Procedure for the Determination of Zinc by Colorimetry

The following is a brief description of the procedure and technic developed, starting with a solution of zinc salt which was freed from all but small amounts of other metals, and made up to a definite known volume.

In a typical experiment the various samples of zinc solution were added to

a series of 50-c.c. Nessler tubes containing about 25 c.c. of alcohol. In the case of the unknown samples amounts were taken which would fall somewhere in the range 0.003 to 0.006 mg., and in the case of the standards a series of eight samples were taken which contained 0.001 to 0.008 mg. in units of 0.001 mg. The standard solution of zinc was made up by dissolving a known amount of pure zinc metal in acid and diluting it to such a volume that 1 c.c. contained 0.01 mg. The solution was slightly acid (owing to an excess of acid used in dissolving the zinc) as were also the solutions of the unknowns. More alcohol was then added, and 1 c.c. of the standard solution of urobilin; the tubes were then made up to the mark with alcohol, and mixed by pouring the solutions to and from a small flask. The solutions were pink in color, owing to the slight acidity of the zinc solutions added.

A drop of concentrated ammonia was added to each tube to render the solutions alkaline. The accurate comparison of standards and unknowns was most reliable when the tubes were allowed to stand for the same length of time, and therefore the solutions were made ammoniacal and shaken well at approximately the same time. The addition of the ammonia and mixing causes the solution to become yellow and the green fluorescence to develop immediately. The solutions of the unknown, on standing ten to twenty minutes after the addition of ammonia, were compared with the standards, readings being taken to one-fourth of the unit division (0.001 mg.). The readings were never made before the solutions had been allowed to stand for five to ten minutes, nor later than twenty to thirty minutes after they had been made ammoniacal, although with the purest alcohol the colors were stable and showed no change of intensity over longer periods of time. The concentration of zinc in the unknown samples was easily calculated by the dilution factor. Determinations were made in duplicate.

The accuracy of the method depends on the readings, which can be made with a limiting error of 10 per cent., and on the effectiveness of the preparation of the solution to be tested; for it is obvious from the foregoing discussion that, unless the zinc is isolated and freed from other metals, interference in the test will occur. I shall now turn to a discussion of the procedure developed for the preparation of the samples to be determined.

V. Isolation of the Zinc for Analysis

A. Discussion.—Practically all common organic materials, vegetable and animal products, contain zinc in varying but appreciable amounts. In such materials the zinc is bound up with the organic material and invariably many other metals occur with it, including large amounts of calcium, magnesium, iron, sodium, and potassium, and smaller amounts of manganese, copper, and nickel. Thus any procedure to isolate the zinc must involve a destruction of the organic material and a chemical separation of the metals. Wet ashing, the usual method employed heretofore in obtaining the inorganic substances free from organic matter, was discarded in

favor of a method of dry ashing at a black to a barely perceptible dull red heat. The method has been studied at length by Dr. P. K. Thompson, and the results which will be discussed in this paper are in accord with and confirm the conclusions reached on the basis of her work in this field.[4]

The sample was first thoroughly dried over a hot plate and partially charred. The dish containing the sample was then placed in an electric furnace and heated at a temperature which was never allowed to rise above a barely perceptible red heat (450° to 550°). When the ash was gray or white, it was extracted with a minimum of 6N hydrochloric acid, and if the ashing was found to be incomplete, the residue on the filter was reashed, using, if necessary, powdered potassium nitrate to burn the last traces of carbon. Through this procedure the organic matter was easily and completely removed without appreciable loss of zinc.

From the discussion of the difficulties inherent in the test with urobilin it is obvious that the substances associated with the zinc in the ash extract (usually large in amount relative to the amount of zinc) must be removed. It is impractical to attempt to precipitate out completely (to 0.005 mg.) calcium and magnesium, in amounts on the order of 1 gm., from 0.01 mg. of zinc, for not only would it be almost impossible to precipitate completely the calcium and magnesium, and utterly impossible to remove large amounts of the alkali metals by precipitation, but it would also be extremely difficult to prevent the loss of a large part of the zinc through adsorption or inclusion by the precipitated metals. The only feasible method suggested was the precipitation of the zinc from a solution containing practically all of the undesirable impurities.

There are several possible methods for the quantitative precipitation of zinc but it seemed hopeless to attempt to carry out any direct procedure involving only 0.01 mg. of material; therefore, a method was devised to make use of the usual sulphide precipitation in weak acid solution (acetate and acetic acid) where a relatively large amount of some metal readily precipitated by hydrogen sulphide in strong acid solution (0.2N) was used to carry down completely this minute amount of zinc, thus making quantitative collection on a filter a relatively simple matter.

It was found that small amounts of zinc (0.01 mg.) were completely precipitated with relatively large amounts of copper but were not completely precipitated alone. The mechanism probably involves the adsorption of one colloidal substance upon the precipitating substance. This carrying down of traces of one substance by another has been employed to good advantage in the work on the toxicology of lead (15). The phenomenon has been called "entrainment" (16), a term which I shall use in this paper and which I shall modify to "entrainer" to refer to that metal which carries down by adsorption, or by mechanical means, the traces of zinc which are being precipitated from solution. If one first removed those metals which would interfere (*i.e.*, iron, which would precipitate as phosphate

[4] A critical study of dry ashing, which will be published shortly.

under these conditions), such a procedure would yield a precipitate containing zinc and the metals precipitated by hydrogen sulphide in acid solution, and thus in one step would remove all of the soluble alkali and alkaline earth elements as well as the acid radicals. The method was developed along these lines and involved as a final step the precipitation in strong acid of the metal added, and the collection of the filtrate containing only the zinc. An account of the procedure follows.

B. General Procedure for the Separation of Zinc.—The extraction of the ash was made with 1 c.c. of 6N hydrochloric acid, and the residue was washed quantitatively. It should be stated concerning the quantities of reagents and dilutions that they are dependent to a certain extent on the amount of sample, impurities, and zinc content; hence the average procedure will be outlined and the special changes discussed in connection with the specific results. A typical sample of an ash extract, artificially prepared, and containing inorganic substances in amounts approximately proportional to those found in normal human feces, was used in testing the method and was of such a composition that a 10-c.c. sample contained the following amounts of substances:

	mg.
Zinc	0.1
Nickel	0.002
Copper	0.2
Manganese	0.2
Iron	1.0
Magnesium	15.0
Calcium	75.0
Ammonium phosphate	50.0

The acid ash solution and washings were collected in a 25-c.c. or 50-c.c. pyrex Erlenmeyer flask and treated with bromine water to oxidize the iron, the excess of bromine being expelled by boiling the solution for several minutes. On cooling, the solution was made up to a volume of about 10 to 20 c.c. and treated with sodium or ammonium acetate until neutral to methyl orange. A distinct turbidity appeared, due to a precipitate of ferric phosphate, and the solution was filtered through a 4-cm. filter paper. In the cases where the amount of iron was large, as evidenced by the rapid flocculation of the precipitate, the phosphate was redissolved in a minimum of 6N hydrochloric acid and reprecipitated (adding an excess of phosphate to the solution); the filtrate was either combined directly with the filtrate from the first precipitation, or treated separately and the sulphide precipitates united. This latter procedure was often followed when there were present large amounts of calcium, magnesium, and phosphate, as was the case in bone and at times in feces. This double precipitation is necessary when large amounts of iron are present, for appreciable amounts of zinc, up to 10 per cent., may be carried down and lost.

To this acetate-acetic acid solution was added 0.5 mg. of copper in the form of a standard solution of copper acetate. This metal acted as the entrainer to precipitate the zinc quantitatively. Hydrogen sulphide was passed into the solution until the precipitation was complete and the copper sulphide had coagulated in large flocculations at the bottom of the flask. The zinc sulphide, insoluble in acetate and acetic acid solution, was carried down quantitatively by the copper

sulphide. The precipitate was filtered through a 4-cm. filter, washed carefully in order to free the sulphides from all traces of contaminating salts, and the filter transferred to the original flask to which traces of copper sulphide adhered tenaciously. The filter and precipitate were treated with a small amount of 6N nitric acid (0.2 to 0.5 c.c.), the acid being heated almost to boiling and the mixture agitated until all of the sulphides were dissolved. The solution was separated from the filter shreds and sulphur by filtration.

In some cases where amounts of calcium and magnesium were large, it was found that these metals precipitated slowly from a saturated solution during and after the filtration of the ferric phosphate; therefore in these cases the nitric acid solution of the sulphides was neutralized with sodium acetate, the zinc and metals of the copper group (17)[5] were reprecipitated as sulphides and, after filtering, treated as before with nitric acid. The solution of zinc and the entrainer collected in a 50-c.c. flask was evaporated just to dryness, and the residue was taken up with 6N hydrochloric acid and again evaporated just to dryness, care being taken in every such case not to overheat the residue. This evaporation with hydrochloric acid served to destroy the nitric acid which would tend to react with hydrogen sulphide to form sulphur in the subsequent precipitations. It should be noted here that the evaporations to remove excess of acids avoided contaminating the solutions with neutral salts which, in even moderate amounts, interfered in the test for zinc with urobilin.

The residue of chlorides of the zinc and metals of the copper group were then dissolved in 0.2 c.c. of 6N hydrochloric acid and 5 c.c. of distilled water, and treated with hydrogen sulphide until the metals of the copper group were completely precipitated and had coagulated, the acid concentration used being sufficient to hold all of the zinc in solution. The filtrate containing the zinc, together with the washings, was collected quantitatively in a 50-c.c. flask and evaporated carefully almost to dryness, so that the trace of acid left caused the solution obtained from the residue to be slightly acid in reaction. The residue was dissolved in a definite volume of water (conveniently proportional to the amount of zinc present) added directly to the flask, or was extracted and diluted to a definite volume in a volumetric flask. Thus a solution of known volume of the sample of zinc was obtained from which samples of definite volumes were removed by means of a graduated pipette for analysis (as described above) with urobilin.

As has been emphasized, the solution obtained by this procedure is free from all interfering substances,[6] but it must be recognized that the proce-

[5] Referring to the classification given by A. A. Noyes in his system of "Qualitative Chemical Analysis."

[6] The procedure has not taken into account the traces of nickel and manganese usually present in materials of organic nature, but inasmuch as these impurities occur in small amounts relative to the amount of zinc present, their effect on the final test is negligible, as has been shown in the discussion of Table 1.

dure is long and involves several steps in which it would be possible to lose appreciable amounts of zinc, such as in the completeness of precipitation of the sulphides, and in the loss due to occlusion and inclusion. Moreover, there is also the chance for contamination by zinc through reagents, glassware, and filter papers. The efficiency of recovery of known amounts of zinc and the analyses of blank solutions were studied in order to obtain an answer to these questions.

VI. Discussion of Results

A number of experiments were carried out to test the method and to show that from a solution of zinc all of the zinc could be recovered using such a procedure as that outlined above. Then, in order to introduce conditions resembling more closely the conditions met with in actual experiments, an artificial ash solution (as described) was used and the efficiency of recovery studied. Several metals, principally cadmium and copper, were used as entrainers to carry down the zinc; the metal finally chosen as the most reliable was copper.

In Table 2 are given the results of a series of preliminary experiments using a relatively large amount of zinc (1 mg.) and varying the entrainer and the concentrations during precipitation. The solutions, made up from a standard solution of pure zinc acetate and a definite amount of the entrainer, were subjected to the final step only of the general procedure—namely, the precipitation of the entrainer from an acid solution of zinc. The effect of the concentration of the hydrogen ion was studied by varying the total volume of the solution and using a constant amount of 6N hydrochloric acid (1 c.c.) in the various volumes listed.

TABLE 2.—RECOVERY OF ZINC FROM SOLUTIONS CONTAINING 1 MG.

ENTRAINER[1] (10 MG.)	VOLUME OF SOLUTION	ZINC FOUND
	c.c.	*mg.*
Cd	15	1.00
Cu		1.00
Cu		1.00
Cd	30	1.00
Cd		0.88
Cu		1.00
Cu		1.00
Cd	40	0.94
Cd		0.88
Cu		1.00
Cu		1.00
Cd	20	1.00
Cd		1.00
Cu		1.00
Cu		1.00

[1] The entrainer is that metal which was used in excess to carry down the zinc by entrainment ((15) (16); see also page 280) during precipitation with hydrogen sulphide in acetate-acetic acid solution.

The metal used as entrainer and the amounts of zinc recovered are listed in respective columns. Using copper as the entrainer, the recoveries were found to be practically 100 per cent., but with cadmium there seemed to be loss in several cases, due probably to occlusion of zinc sulphide in the precipitate of cadmium sulphide.

In several experiments listed in Table 3 the general procedure was modified by using 5.5-cm. filter papers and larger volumes of solutions. The amounts of zinc found were high and a number of blank experiments (Table

4) which were carried out under the same conditions on solutions containing no zinc showed that there was being introduced a roughly constant amount of zinc. By carrying out several experiments in platinum and quartz it was shown that the evaporation of acids in glass was not responsible for the introduced error. A constant correction based on these blank experiments was applied in Table 3, and the amount of the zinc added that was actually recovered was calculated. The results listed in Tables 2 and 3 show conclusively that the method is efficient in the recovery of zinc from solutions of its salts.

TABLE 3.—RECOVERY OF ZINC FROM KNOWN ZINC ACETATE SOLUTIONS

AMOUNT OF ZINC IN SAMPLE	EN-TRAINER (10 MG.)	TOTAL ZINC FOUND	AMOUNT OF ZINC RECOV-ERED[1]
mg.		*mg.*	*mg.*
0.05	Cd	0.060	0.045
.10	Cd	.125	.110
.10	Cu	.113	.098
.50	Cu	.500	.485
.10[2]	Cd	.125	.110
.10[2]	Cd	.125	.110

[1] Correction for error introduced by reagents as determined by blank experiments, 0.015 mg. (see Table 4).

[2] Artificial ash solutions.

A series of experiments was made on the various metals of the copper group (Table 5) to determine their efficiency as entrainers for zinc. The results showed that all of them (copper, cadmium, bismuth, and lead) could be used successfully. The most convenient metals of the group were copper and cadmium, but inasmuch as cadmium gave low results in several cases (see Tables 2 and 6), copper was selected as the more reliable and efficient entrainer.

TABLE 4.—BLANK EXPERIMENTS[1] TO DETERMINE CONSTANT ERROR OF METHOD

(*5 mg. of copper used as entrainer; no zinc added*)

SOLUTION	ZINC FOUND
	mg.
Blank	0.012
	.016
	.015
	.013
	.019
	.019
Artificial ash	.016
	.016
	.013
	Av. 0.015
Blank[2]	.020
Artificial ash[2]	.020
Blank[3]	.010
	.008
Artificial ash[3]	.015
	.012

[1] Used filter papers size 5.5 cm. Double precipitation of iron.

[2] Carried out in platinum.

[3] Carried out in quartz.

Several experiments were carried out (Table 6) to recover 0.1 mg. of zinc where different concentrations of hydrochloric acid were used in the final precipitation of the copper and the cadmium. Little effect was observed except in the case of cadmium where there was a definite loss when the hydrogen-ion concentration was high (actually when the volume containing the given amount of acid was low). Only the final step in the general procedure was studied and the

blank experiments were lower than those found and considered in Table 4.

In Table 7 are listed the results of several experiments on the zinc content of the reagents, distilled water, and filter papers, and the results show that, although the zinc present was very small in amounts, it was not wholly negligible as a factor affecting the results obtained by this method. In the filter papers tested, the largest amounts of zinc were found in the no. 5 filters, in amount six times that found in the best grade (no. 40). This fact serves to demonstrate the importance of using only the best, chemically treated filter papers in this type of work. The results given in Table 9 on the analyses of no. 40 filter papers check with the results given in Table 7.

So far the correction for blank experiments, to which no zinc was added, has been so large as to render the test with urobilin useless for determining amounts of zinc as low as 0.01 mg. The general procedure as outlined, however, involved a correction of only 0.0035 mg., as was determined in the series of recoveries listed in Table 9. The high correction used in the foregoing results was due to the larger amounts of reagents, larger filters, and larger volumes of solutions which were used in the preliminary work before the final method was worked out to minimize this error. When an amount of zinc as low as 0.01 mg. was being considered, the general method was reduced to a microchemical scale where small volumes of substances and 3-cm. filter papers were used. The volume of solution was never allowed to exceed 5 to 10 c.c., and the final precipitation of the

TABLE 5.—USE OF METALS OF COPPER GROUP AS ENTRAINERS[1]

(Zinc present, 0.1 mg.)

ENTRAINER (10 MG.)	TOTAL ZINC FOUND	AMOUNT OF ZINC RECOVERED
	mg.	*mg.*
Cd	0.115	0.100
Cd	.115	.100
Cd	.118	.103
Cu	.108	.093
Cu	.110	.095
Cu	.107	.092
Bi	.109	.094
Bi	.117	.102
Pb	.131	.116
Pb	.128	.113

[1] Double precipitation of iron. Correction for error introduced by reagents, 0.015 mg. (see Table 4).

TABLE 6.—EFFECT OF HYDROGEN ION CONCENTRATION ON PRECIPITATION OF ENTRAINER

(1 c.c. of 6N hydrochloric acid and 0.1 mg. of zinc were used in each experiment)

ENTRAINER (10 MG.)	VOLUME OF SOLUTION	TOTAL ZINC FOUND	AMOUNT OF ZINC RECOVERED
	c.c.	*mg.*	*mg.*
Cd	35	0.100	0.091
Cd		.108	.099
Cu		.110	.101
Cu		.110	.101
Cd	15	.100	.091
Cd		.100	.091
Cu		.110	.101
Cu		.110	.101
Cd	10	.080	.071
Cd		.080	.071
Cu		.100	.091
Cu		.100	.091
Cd[1]	25	.009	....
Cd[1]		.010	....
Cu[1]		.007	....

[1] Blank experiments. Average value (0.009 mg.) used as correction.

copper was carried out in 2 c.c. of water containing 0.1 c.c. of 6N hydrochloric acid. The results listed in

TABLE 7.—DETERMINATION OF ZINC IN VARIOUS REAGENTS

(2 mg. of copper used as entrainer)

MATERIAL	AMOUNT	TOTAL ZINC FOUND	AMOUNT OF ZINC FOUND (CORRECTED)[1]	ZINC CONTENT
	l.	*mg.*	*mg.*	*mg.*
Distilled water	5	0.070	0.061	0.010 per liter
Distilled water	5	.050	.041	
	c.c.			
Concentrated HCl	500	.018	.009	.002 per 100 c.c.
Concentrated HCl	500	.020	.011	
	gm.			
$Cd(NO_3)_2 \cdot 4H_2O$	5	.025	.016	.004 per gram
$Cd(NO_3)_2 \cdot 4H_2O$	5	.028	.019	
$CuSO_4 \cdot 7H_2O$	10	.028	.019	.002 per gram
Sodium acetate	20	.023	.014	.007 per 10 gm.
Sodium acetate	20	.023	.014	
	sheets			
9 cm. filter[2] paper ⅋40	10	.020	.011	.001 per sheet
5.5 cm. filter[2] paper ⅋41	12	.020	.011	.001 per sheet
9 cm. filter[2] paper ⅋5	10	.060	.051	.006 per sheet
9 cm. filter[2] paper ⅋5	10	.060	.051	

[1] Correction, 0.009 mg.

[2] Whatman filter papers used.

Table 8 proved that the method was successful and could be applied to the analysis of organic materials, as was done in a specific instance in the analysis of soluble starch, where the zinc content of the material checked with the value found and given in Table 9. The recoveries of zinc added were quantitative.

The results on which the general procedure and technic were based are given in Table 9. A number of typical materials of organic nature, food products including starches, flours, a cereal, milk, yolk of egg, and animal products, blood and feces, were analyzed for zinc by dry ashing and following in detail the general procedure as I have outlined it above. Parallel experiments were made to recover zinc added to these materials in the form of the acetate. After applying the constant correction and subtracting the zinc content of the materials analyzed, the actual amounts recovered of the zinc added were obtained. These are listed in Table 9. In this series of analyses the method has received a thorough testing out

with regard to the efficiency of recovery of zinc from a variety of organic materials, and the success of the method as defined in the foregoing account is demonstrated.

It is of interest to note that the results of the analyses are in accord with results obtained by other investigators, using the turbidimetric method with potassium ferrocyanide, and that this agreement is a rough corroboration of the effectiveness of the two methods. The amount of zinc found in cow's blood by the method I have discussed was 5.1 mg. per kilogram, and agrees with the value, 5.5 mg. per kilogram, determined by Weitzel using the turbidimetric method (18). The figures given by Weitzel for human feces, when calculated on the bases of weight of fresh material, agreed approximately with the value calculated from the results in Table 9. The amount of zinc found in samples of the yolk of an egg was 26.2 mg. per kilogram and proved to be slightly more than half the value obtained by Birckner (19). In this laboratory commercial samples of cornstarch, "Klim" (powdered milk), and flour, were analyzed by Dr. P. K. Thompson[7] using the ferrocyanide turbidimetric method, and the amounts of zinc found per 100 gm. were respectively 3.7 mg., 2.5 mg., and less than 0.1 to 0.3 mg. These results are in complete accord with the results given in Table 9 where analyses of samples using the urobilin method yielded per 100 gm. for cornstarch, 3.5 mg.; for "Klim," 2 mg.; and for flour, 0.08 mg.

In the case of the analyses of flour the line is observed between the applicability of the ferrocyanide method and the method that I have developed in this paper, for the former fails to detect a trace of zinc below 0.2 to 0.3 mg., whereas the latter method is capable not only of determining these amounts quantitatively within a limiting error of about 10 per cent., but also of employing one-twentieth of the amounts of samples of the materials to be analyzed. An investigation is now in progress in this laboratory, utilizing the urobilin

TABLE 8.—RECOVERY OF ZINC FROM SOLUTIONS

(Determinations involving quantities of the order of 0.01 mg. of zinc, and carried out on a microchemical scale. 0.2 mg. of copper used as entrainer)

MATERIAL	ZINC ADDED	TOTAL ZINC FOUND	AMOUNT OF ADDED ZINC RECOVERED
	mg.	*mg.*	*mg.*
Blank	...	0.002	....
	...	.002	....
	...	.001	....
		Av. 0.0017	
Artificial ash	0.010	.010	0.0083
	.010	.010	.0083
	.010	.012	.010
	.015	.017	.015
Soluble starch	....	.006	....
	....	.004	....
		Av. 0.005	
	.010	.014	.009
	.010	.015	.010
	.030	.035	.030
	.050	.055	.050
	.050	.055	.050

[7] Unpublished results.

TABLE 9.—RECOVERY OF ZINC FROM TYPICAL MATERIALS

(0.5 mg. of copper used as entrainer)

MATERIAL USED	ZINC ADDED	TOTAL ZINC FOUND	AMOUNT OF ZINC, CORRECTED FOR CONSTANT ERROR	AVERAGE NORMAL ZINC CONTENT OF MATERIALS	AMOUNT OF ADDED ZINC RECOVERED
	mg.	*mg.*	*mg.*	*mg.*	*mg.*
Filter paper # 40, 9 cm. (6 sheets)	...	0.009	0.006	0.006	....
	...	.009	.006		....
	0.10	.087	.084		0.078
	.10	.088	.085		.079
	.10	.106	.103		.097
	.15	.153	.150		.144
	.20	.200	.197		.191
Soluble starch (5 gm.)	...	.020	.017		....
	...	.015	.012	.015	....
	...	.020	.017		....
	.10	.100	.097		.082
	.10	.121	.118		.103
	.15	.147	.144		.130
	.15	.161	.158		.143
	.20	.217	.214		.199
Cornstarch (5 gm.)	...	.180	.177	.175	....
	.02	.205	.202		.025
	.04	.225	.222		.045
Flour (5 gm.)	...	.010	.007		....
	...	.006	.003	.004	....
	...	.006	.003		....
	.10	.100	.097		.093
	.10	.108	.105		.101
	.20	.212	.209		.205
Graham flour (5 gm.)	...	.020	.019	.019	....
	.02	.042	.040		.021
Wheatena (10 gm.)	...	.310	....	.310	....
	.04	.350	....		.040
	.08	.400	....		.090
Yolk of egg (5 gm.)	...	.135	.130	.131	....
	...	.135	.132		....
	.05	.178	.175		.044
	.10	.235	.232		.101
"Klim" (5 gm.)	...	.103	.100	.098	....
	...	.100	.097		....
	.06	.150	.147		.049
	.10	.190	.187		.089

TABLE 9.—*Continued*

MATERIAL USED	ZINC ADDED	TOTAL ZINC FOUND	AMOUNT OF ZINC, CORRECTED FOR CONSTANT ERROR	AVERAGE NORMAL ZINC CONTENT OF MATERIALS	AMOUNT OF ADDED ZINC RECOVERED
	mg.	*mg.*	*mg.*	*mg.*	*mg.*
Human[1] feces (5 gm.)	...	.525	.522	.510	....
	...	.525	.522		....
	.10	.625	.622		.100
	.10	.625	.622		.100
	.20	.733	.730		.208
Cow's blood (5 c.c.)	...	.030	.027	.025	....
	...	.030	.027		....
	.02	.045	.042		.015
	.02	.050	.048		.021
	.05	.075	.072		.045
Blank on reagents	...	.004	....	.0035	....
	...	.0045	....		....
	...	.002	....		....

[1] Double precipitation of iron, a double amount of copper used as precipitant.

method to study the distribution of zinc in animal organisms, both in cases of normal contact with zinc (in foods, water, etc.) and in cases where zinc is introduced abnormally in various ways and forms.

VII. Summary

A method has been developed, capable of determining with an accuracy of 10 per cent. amounts of zinc ranging from 0.01 mg. to 0.5 mg., utilizing the fluorescence produced by the action of zinc salts on urobilin. The method used for the preparation of urobilin and the complete general procedure for the analysis of a typical sample are outlined. The analysis for zinc involved ashing of material, isolation of the zinc through precipitation by means of an entrainer, and colorimetric deter-

mination by comparison with standards. The results obtained in several series of recoveries by which the method was developed and studied, and the applicability and limitations of the method, are discussed critically.

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BOOK REVIEWS

Skill in Work and Play. By *T. H. Pear*, M.A., B.Sc., Professor of Psychology in the University of Manchester; Fellow of King's College, London; Author of "Remembering and Forgetting." Cloth. Pp. 107, with illustrations and index. New York: E. P. Dutton and Company, 1924.

The purpose of this small volume is to "discuss the various ways in which muscular skill is, and might be, acquired by persons of different types of mentality, under various circumstances. . . . . .

"The choice of title seems justifiable in view of the fact that some people play at their work while others work at their play. Facts discovered in connexion with the swinging of golf clubs may be applicable to the swinging of picks, and some of the laws governing the effective use of the sledge-hammer have been shown to operate in the less Herculean task of covering creams with chocolate. Any industrialist who considers athletic sports unimportant may, if he likes, skip the illustrations taken from games; the open-air athlete may avoid if he chooses, those paragraphs containing the word industry or its derivatives. But then they will find this book more difficult reading than the writer meant it to be. For Nature abhors labels, and the difference between work and play lies in the spirit in which we move and think."

The author thus makes an attractive introduction for a book which unfortunately must leave most of us in a rather vague state of mind. It is, however, fair to say that this situation is due rather more to defects in human knowledge than to the author's efforts at exposition.

The first chapter deals with the difficulties of describing muscular experience. We observe that one person performs a muscular act far better than another, but it is a most exceptional gift to be able to describe why this is so, nor can the skilled performer give an adequate analysis of his performance. We are comparatively well equipped for describing experiences interpreted through other senses, but our vocabulary for describing what may be called muscle sensations is most deficient. Thus, at the very beginning of an inquiry into skill in work and play, a serious handicap is

met. One knows that proficiency exists. One can evaluate it in games won or in piecework finished, but one cannot describe the elements which bring about this success.

In the second chapter, on "Acquiring Skill," difficulties grow more apparent. Skill is provisionally defined as "an organization and integration. . . . 'For the most part, of bodily habits.'" And the most relevant aspects of habit seem to be:

"(1) That it is a definite series of bodily movements gradually acquired in answer to a definite external situation.

"(2) That these movements are performed with less effort and less attention than are non-habitual movements."

The author does not believe that certain persons possess from birth an instinct for skilled muscular performance. The acquisition of skill apparently consists in the intelligent and persistent use and correlation of movements previously learned or, in rarer instances, of movements quite novel to the individual. Most opinions as to the acquisition of physical dexterity lean toward the idea that it is acquired blindly, that the athlete or the workman tries many different ways and finally, almost without knowing it, hits upon the smooth and economical line of perfect accomplishment. Such a conception of muscular proficiency practically invariably leaves out the degree of introspection and self-examination which has filled the life of the subject during his period of learning. If it were not for our difficulty in analyzing and reporting muscular sensations, the intellectual aspects of acquiring skill and teaching skill would stand more prominently than our confidence in the rough processes of trial and error.

The third chapter deals with the general methods which have been used in the investigation of learning. The transition from Taylor's emphasis on factors which make for speed to the modern belief in concentrating on ease and economy of movement is well summarized.

"The essence of this belief is that more benefit will come from concentrating upon the *ease* with which a worker can perform a movement than upon his *speed*. The centre of attention is not to be so much the task as the effort of the worker. It is more important to study the worker than the work, and the following aims should direct such study:

"(1) Body and mind should be used in the most economical way, by avoiding all possible strain of the muscles and of the nervous system.

"(2) The new method should meet with the approval of the workers, as a result of their understanding its nature and giving it a fair trial. It should make them feel less tired and more satisfied with their work."

Instances of the value of discerning and constructive training in simple industrial performances are now given and are followed by an analysis of methods of training in and of the selection of trainers for muscular work. The presentation is brief but it is exceedingly suggestive. The inclusion of a limited number of references is appropriate in a book so stimulating to thought and inquiry.—*Cecil K. Drinker.*

THE VENTILATION OF SCHOOL BUILDINGS. A STUDY OF PRESENT PRACTICES AND COSTS IN THE LIGHT OF EXPERIMENTAL RESEARCH. By *John Rankin McLure*, Ph.D., Professor and Head of Department of School Administration, School of Education, University of Alabama. Cloth. Pp. vii, 130 with illustrations and bibliography. New York: Teachers College, Columbia University, Contributions to Education, No. 157, 1924.

This book leaves the reader with a strong impression that the best method for schoolroom ventilation is by window, with gravity or fan exhaust. Essentially it is in strong support of the conclusions of the New York State Commission on Ventilation, whose report is quoted continually.

The first chapter, twenty-four pages, is devoted to "Changing Conceptions of Ventilation," in which the chronological development of ventilation methods and principles is traced from the old "poisonous carbon dioxide" theory, through the "toxic organic poisons in expired air" down to the modern views of heat stagnation. In this chapter, as in all those following, the author uses many quotations and references. In fact, the book is a distinct contribution for its bibliography alone.

In Chapter II, six pages, he reviews the state laws for schoolroom ventilation, and shows that, of those states having such laws, practically all have copied them from the original passed by Massachusetts, in which 30 cubic feet per minute per pupil was required. This state, he claims, had little or no grounds on which to pass the law, which many other states have as unreasonably copied.

Chapter III, forty-two pages, is devoted to a discussion of data collected by the author on ventilation installations in the schools of ninety-six cities with populations over 30,000. He concludes that the mechanically operated systems do not fulfill their intended purpose of regular and even air distribution, that they are inadequate with respect to temperature control, and that the 30 cubic feet law "operates to prevent the application of new knowledge to the problem of school building ventilation."

The most serious indictment of mechanical ventilation occurs in Chapter IV, twenty-nine pages, Chapter V, seven pages, and Chapter VI, five pages, in which Dr. McLure endeavors to show that typical mechanical ventilation installations are not justified by the amount they are used, and that they are needlessly expensive when in use, and positively wasteful, since they lie idle during the months when heat is not required.

This book is very refreshing in both its subject and style of presentation. While it is regrettable that too few copies were printed to render its wide circulation possible, it is hoped that there are sufficient available for use in the libraries of our cities and universities.—*Philip Drinker.*